Topic 8: Redox Chemistry and Groups 1, 2 and 7

8A: Redox chemistry

Students will be assessed on their ability to:

8.1	know what is meant by the term ‘oxidation number’ and understand the rules for assigning oxidation numbers

Monoatomic ion means an ion consisting of one atom

Oxidation number is the charge that an ion has, or the change it would have if the species were fully ionic

Rules for assigning oxidation numbers:

The oxidation number of any uncombined element (Free state) is zero	H_2, Zn, O_2
Sum of the oxidation numbers of all the elements in a neutral compound is zero	In NaCl, Na = +1, Cl = -1 Sum = +1-1 = 0
The oxidation number of any *monoatomic ion* is equal to its ionic charge	Zn^{2+} = 2+ Fe^{3+} = 3+
Sum of the oxidation numbers of all the elements in an ion is equal to the charge on the ion	SO_4^{2-} Oxidation no. of S = +6 Oxidation no. of O = 4x-2 Sum = -2
The more electronegative element in a substance is given a negative oxidation number	F_2O, as F is more electronegative, F = 2x -1 O = +2
Gp.1 elements are always +1 Gp.2 elements are always +2 Fluorine is always +1 Hydrogen is +1, except when combined with a less electronegative element (i.e. in metal hydroxides) Oxygen is -2, except in peroxides where it is -1 and when combined with fluorine where it is +2	Li^+ Mg^{2+}

8.2	be able to calculate the oxidation number of elements in compounds and ions, including in peroxides and metal hydrides

Eg. of metal hydrides: NaH

Hydrogen atom is present as a hydride ion, H^-

Eg. of peroxides: hydrogen peroxide, H_2O_2

Oxygen must have an oxidation state of -1

8.3	be able to indicate the oxidation number of an element in a compound or an ion, using a Roman numeral

When the element has a variable oxidation number, the number is written afterwards in ROMAN numerals

In IUPAC convention, the various forms of sulfur, nitrogen and chlorine compounds where oxygen is combined are all called sulfates, nitrates and chlorates with relevant oxidation number given in roman numerals.

If asked to name these compounds remember to add the oxidation number:

NaClO: sodium chlorate(I)	K_2SO_3: potassium sulfate(IV)
$NaClO_3$: sodium chlorate(V)	$NaNO_3$: sodium nitrate(V)
K_2SO_4: potassium sulfate(VI)	$NaNO_2$: sodium nitrate(III)

8.4	be able to write formulae given oxidation numbers

8.5 understand oxidation and reduction in terms of electron transfer and changes in oxidation number, and the application of these ideas to reactions of *s*-block and *p*-block elements

Oxidation	Reduction
Addition of Oxygen	Loss of Oxygen
Loss of Hydrogen	Addition of Hydrogen
Loss of electrons	Gain of electrons

Balanced equation: $Mg(s) + CuSO_4(aq) \rightarrow MgSO_4(aq) + Cu(s)$

$$Mg(s) + Cu^{2+}(aq) + \cancel{SO_4^{2-}}(aq) \rightarrow Mg^{2+}(aq) + \cancel{SO_4^{2-}}(aq) + Cu(s)$$

Ionic equation:

oxidation (reducing agent)

$$Mg(s) + Cu^{2+}(aq) \rightarrow Mg^{2+}(aq) + Cu(s)$$

reduction (oxidising agent)

$Mg \rightarrow Mg^{2+} + 2e^-$ $\qquad$ $Cu^{2+} + 2e^- \rightarrow Cu$: Half equation

Mg loses electrons so it has been oxidized
The *reducing agent* is the Mg as it is an *electron donor*
Oxidation no. of reducing agent increases

Cu^{2+} gains electrons so it has been reduced
The *oxidising agent* is the Cu^{2+} ion as it is an *electron acceptor*
Oxidation no. of oxidising agent decreases

S-block (consisting mainly of metals) generally form positive ions by losing electrons with an increase in oxidation number
P-block (consisting mainly of non-metals) generally form negative ions by gaining electrons with a decrease in oxidation number

8.6 know that **oxidising agents gain electrons** and **reducing agents lose electrons**

8.7 understand that **a disproportionation reaction involves an element in a single species being simultaneously oxidised and reduced**

CHANGE IN OX No = +1
ONE Cl ATOM HAS BEEN OXIDISED

$$\underset{0}{Cl_2} + \underset{+1\ -2}{H_2O} \longrightarrow \underset{+1\ -1}{HCl} + \underset{+1\ +1\ -2}{HClO}$$

CHANGE IN OX No = −1
ONE Cl ATOM HAS BEEN REDUCED

8.8 know that oxidation number is a useful concept in terms of the classification of reactions as redox and as disproportionation

A ***redox reaction*** is a reaction in which both oxidation and reduction are simultaneously occurring at the same time
A ***disproportionation reaction*** is a reaction in which a single species is being simultaneously oxidized and reduced at the same time

8.9 understand that **metals, in general, form positive ions by loss of electrons with an increase in oxidation number** whereas **non-metals, in general, form negative ions by gain of electrons with a decrease in oxidation number**

8.10 be able to write ionic half-equations and use them to construct full ionic equations

8B: The elements of Groups 1 and 2

Students will be assessed on their ability to:

8.11	understand reasons for the trend in ionisation energy down Groups 1 and 2
8.12	understand reasons for the trend in reactivity of the elements down Group 1 (Li to K) and Group 2 (Mg to Ba)

Color is shown based on flame color

Li	Be
Na	Mg
K	Ca
Rb	Sr
Cs	Ba
Fr	

Ionization energy increase down the group
Reactivity increase down the group

Solubility of Gp. 2 hydroxides increase
Solubility of Gp. 2 sulfates decrease

Mpt & bpt decrease down the gp.

Thermal stability of Gp. 1 and 2 carbonates
and nitrates increase down the group

Ionisation energy increases down the group because:
Increased shielding from inner electrons + larger distance between outermost electron and the nucleus outweigh the increase in nuclear charge
Reactivity increases down the group because:
The outermost electron gets further away from the nucleus so there is increased shielding and weaker forces of attraction which require little energy to overcome

8.13	know the reactions of the elements of Group 1 (Li to K) and Group 2 (Mg to Ba) with oxygen, chlorine and water

<u>Reactions with Oxygen</u>:

General equations for Group 1: $4M(s) + O_2(g) \rightarrow 2M_2O(s)$

Group 2: $2M(s) + O_2(g) \rightarrow 2MO(s)$

<u>Reactions with Chlorine</u>:

General equations for Group 1: $2M(s) + Cl_2(g) \rightarrow 2MCl(s)$

Group 2: $M(s) + Cl_2(g) \rightarrow 2MCl_2(s)$

Observations: A white solid is formed

<u>Reactions with Water</u>:

General equations for Group 1: $2M(s) + 2H_2O(l) \rightarrow 2MOH(aq) + H_2(g)$

Group 2: $M(s) + 2H_2O(l) \rightarrow M(OH)_2(aq) + H_2(g)$

!Note Mg reacts slowly with water to form $Mg(OH)_2$ but reacts vigorously with steam to form a white solid MgO (even producing a bright white flame)

Observations: Fizzing (more vigorous down the group)
Metal getting smaller and disappearing (faster down the group)
Solution getting warmer (exothermic reaction) and is alkaline

8.14	know the reactions of: i oxides of Group 1 and 2 elements with water and dilute acid ii hydroxides of Group 1 and 2 elements with dilute acid

i

Reaction of oxides with water

For Group 1 oxides: $M_2O(s) + H_2O(l) \rightarrow 2MOH(aq)$

For Group 2 oxides: $MO(s) + H_2O(l) \rightarrow M(OH)_2(aq)$

Group 1 and 2 metal (basic) oxides react with water to produce a colorless alkaline solution

ii	Reactions of oxides and hydroxides with acid All of the Group 1 and 2 oxides and hydroxides react with acids in a neutralization reaction to form salts and water Observations: a white solid reacts to form a colorless solution Solution gets warmer (exothermic reaction)
8.15	know the trends in solubility of the hydroxides and sulfates of Group 2 elements
	Solubility of Group 2 hydroxides increase down the group: Magnesium hydroxide is insoluble in water (used in medicine) Calcium hydroxide is reasonably soluble in water (used in agriculture) Barium hydroxide is very soluble
	Solubility of Group 2 sulfates decrease down the group
8.16	understand the reasons for the trends in thermal stability of the nitrates and the carbonates of the elements in Groups 1 and 2 in terms of the size and charge of the cations involved

If compound does not decompose, it is thermally stable

Thermal stability is a measure of the extent to which a compound decomposes when heated (i.e. how stable a compound is when heated)

Thermal Stability of Nitrates

All of Group 1 & 2 nitrates are white solids

When they are heated, they all decompose to nitrites or oxides, and give off nitrogen dioxide (brown fumes) and/or oxygen (and steam too if it contains water of crystallization)

If brown fumes are observed, this indicates a greater decomposition:

metal nitrate → metal oxide + nitrogen dioxide + oxygen

nitrate = nitrate(V)
nitrite = nitrate(III)

If no brown fumes are observed, this indicates a lesser decomposition:

metal nitrate → metal nitrite + oxygen

Group 1

$4LiNO_3(s) \longrightarrow 2Li_2O(s) + 4NO_2(g) + O_2(g)$

The only Gp.1 nitrate that decomposes in the same way as Gp.2 nitrates is Lithium nitrate

The rest of the Gp.1 nitrates decompose in this way:

$2XNO_3(s) \rightarrow 2XNO_2(s) + O_2(g)$

Do note that each have to be at a certain temperature to undergo the reaction

Decomposition of nitrates is done in fume cupboards as nitrogen dioxide is toxic

Group 2

All Gp.2 nitrates decompose in this way:

$2X(NO_3)_2 \rightarrow 2XO + 4NO_2 + O_2$

Greater decomposition occurs when:

- The cation has a 2+ charge (all of Gp.2 nitrates)
- The cation has a 1+ charge and is also the smallest in Gp.1 (i.e. Lithium)

As you go down the group, more heat is needed to break down the carbonate and nitrate ions

Thermal stability of Gp.1 and Gp.2 nitrates increases down the group

- The smaller positive ions at the top of the groups will polarize the anions more than the larger ions at the bottom
- The more polarized they are, the more likely they are to thermally decompose as the bonds in the carbonate and nitrate ions become weaker

The small positive ion attracts the delocalised electrons in the nitrate or carbonate ion towards itself
The higher the charge and the smaller the ion the higher the polarising power

Down the group, both the nitrates & carbonates require more heating to decompose	**Thermal Stability of Carbonates** All of Group 1 and 2 carbonates are white solids. When they are heated, they either do not decompose at all or decompose to oxides and give off carbon dioxide As the gas given off is colorless and both the carbonate and oxide are white solids, no observations can be made **Group 1** Group 1 carbonates do not decompose at Bunsen temperature with the exception of Lithium as it has the smallest size of ion among Gp.1 elements and so it has a greater charge density resulting in it being more polarizing of the C-O bond The rest of the Gp.1 carbonates only have +1 charges and so they don't have a big enough charge density to polarize the carbonate ion. $Li_2CO_3(s) \rightarrow Li_2O(s) + CO_2(g)$ Gp.1 carbonates have more thermal stability than Gp.2 carbonates **Group 2** All Gp.2 carbonates decompose in this way: $XCO_3(s) \rightarrow XO(s) + CO_2(g)$ The thermal stability of Group 2 carbonates increases down the group because as you go down, the size of cation increases but has the same overall charge which means a decrease in charge density of cation down the group. This means the cation is less polarising of the C-O bond (electron cloud of anion is distorted less) This means stronger (C-O) covalent bonds in the carbonate ion, hence more energy required to break the bonds Decomposition occurs when: • The cation has a 2+ charge (all of Gp.2 carbonates) • The cation has a 1+ charge and is also the smallest Gp.1 cation (only lithium carbonate)

8.17	understand the formation of characteristic flame colours by Group 1 and 2 compounds in terms of electron transitions *Students will be expected to know the flame colours for Group 1 and 2 compounds.*

In a flame test, the heat causes the electrons to absorb energy and move to a higher energy level (to its excited state)
The electron is unstable at the higher energy level and so drops back down to a lower energy level, during which energy is emitted in the form of visible light energy with the wavelength of the observed light (colour)

Formula	Colour
Li^+	Red
Na^+	Yellow/orange
K^+	Lilac
Rb^+	Red/purple
Cs^+	Blue/violet
Be^{2+}	No colour
Mg^{2+}	No colour
Ca^{2+}	(Brick) red
Sr^{2+}	(Crimson) red
Ba^{2+}	(apple) green

8.18	know experimental procedures to show: i patterns in the thermal decomposition of Group 1 and 2 nitrates and carbonates *Students will be expected to know tests for carbon dioxide and oxygen; and to recognise nitrogen dioxide by its colour and acidic pH.* ii flame colours in compounds of Group 1 and 2 elements
8.19	know reactions, including ionic equations where appropriate, for identifying: i carbonate ions, CO^{2-}, and hydrogencarbonate ions, HCO^{-} ,using an aqueous acid to form carbon dioxide (and testing the gas with limewater) ii sulfate ions, SO^{2-}, using acidified barium chloride solution iii ammonium ions, NH_4, using sodium hydroxide solution and warming to form ammonia (and testing with litmus and HCl fumes)
i	Add dilute hydrochloric acid to the test tube to be tested Test the gas released by bubbling it through limewater Carbon dioxide produced turns limewater milky
ii	Add dilute hydrochloric acid (or dilute nitric acid) and add barium chloride solution If a sulfate is present, white precipitate (barium sulfate) will be produced
iii	Dissolve the solid salt in distilled water and put it in a test tube Add aqueous sodium hydroxide solution and warm (using a water bath) Test the gas released- Ammonia gas produced turns damp red litmus paper blue (or) you could react the ammonia gas with hydrogen chloride gas (from conc. HCl) white smoke (ammonium chloride) will be produced
8.20	be able to calculate solution concentrations, in mol dm^{-3} and g dm^{-3}, including simple acid-base titrations using the indicators methyl orange and phenolphthalein
8.21	**CORE PRACTICAL 3** **Finding the concentration of a solution of hydrochloric acid.**
8.22	understand how to minimise the sources of measurement uncertainty in volumetric analysis and estimate the overall uncertainty in the calculated result

Readings (one judgement)	Measurement (two judgements)
The values found from a single judgement when using a piece of equipment	The values found as the difference between the judgements of two values Eg: burette in titration
Uncertainty is at least ±1/2 of smallest scale reading	Uncertainty is at least ±1 of smallest scale reading

Apparatus	Capacity	Measurement uncertainty
Burette	$50cm^3$	$\pm 0.05cm^3$ (but since it is read twice(final and initial volume), total measurement uncertainty is 0.05 x 2 = $0.10cm^3$
Pipette	$25cm^3$	$\pm 0.1cm^3$
Volumetric flask	$250cm^3$	$\pm 0.1cm^3$

Calculating percentage uncertainty: $\text{percentage uncertainty } (\%) = \frac{\text{total uncertainty}}{\text{measured value}} \times 100$

How to reduce uncertainties in a titration

- Replace measuring cylinders with pipette or burette which have greater resolution which will lower uncertainty and thus, lower error
- To reduce uncertainty in burette readings, increase the size of measurement (titre) made either by increasing the mass/volume/conc. of the substance in the conical flask or decreasing the volume/conc. of substance in the burette

How to reduce uncertainties in measuring mass

- Use a more accurate balance or a larger mass
- Weigh the sample before and after addition and calculating the difference

8.23	**CORE PRACTICAL 4** **Preparation of a standard solution from a solid acid and use it to find the concentration of a solution of sodium hydroxide.**
	Further suggested practicals: i experiments to study the thermal decomposition of Group 1 and 2 nitrates and carbonates ii flame tests on compounds of Group 1 and 2 iii simple acid-base titrations using the indicators methyl orange and phenolphthalein to calculate solution concentrations in g dm^{-3} and mol dm^{-3} iv the solubility of calcium hydroxide by titration v determination of moles of water of crystallisation by titration
ii	**How to carry out a flame test** - Clean a platinum or nichrome wire by dipping it into concentrated hydrochloric acid and then into a flame until no colour shows - Then, dip the loop of wire into the solid sample and hold it at the edge of a non-luminous blue Bunsen flame

8C: Inorganic chemistry of Group 7 (limited to chlorine, bromine and iodine)

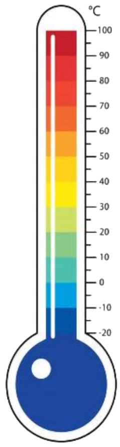
Students will be assessed on their ability to:

8.24	understand reasons for the trends for Group 7 elements in: i melting and boiling temperatures and physical state at room temperature ii electronegativity iii reactivity down the group

	State & Color at rtp	Color in solution
F	Yellow Gas	-
Cl	Pale Green Gas	Pale Green
Br	Red-Brown Liquid (orange vapour)	Orange
I	Grey Solid (Purple vapour)	Dark grey Dark brown
At	Black Solid	

Colors get darker down the gp.

M.pt B.pt



m.pt & b.pt increase down the gp.

Electronegativity/Reactivity

First IE decreases down the gp.

Electronegativity decrease down the gp.

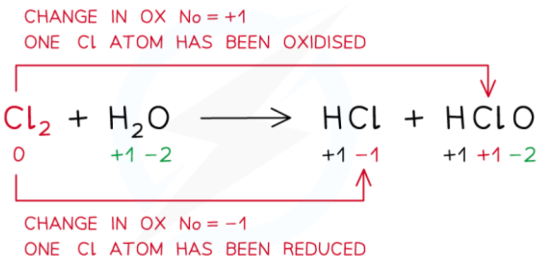
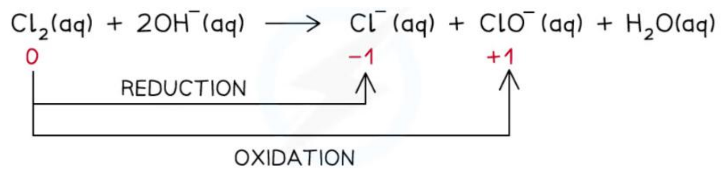
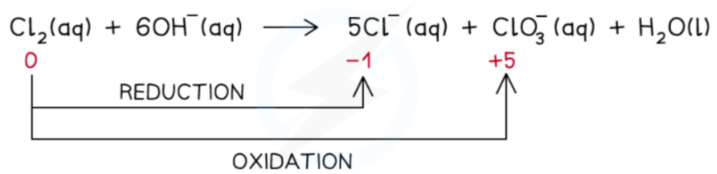
Reactivity decrease down the group

!Note no covalent bonds are broken

i	Halogens are non-metals and exist as diatomic molecules at room temperature and they have weak simple molecular structures Melting and boiling temperatures increase down the group as there are more electrons which results in greater instantaneous dipole-induced dipole forces, in other words stronger London forces between molecules As the strength of intermolecular forces increases, more energy is required to be put in to overcome these forces
ii	Electronegativity decreases down the group as (although the nuclear charge increases) the atomic radii increases due to the increasing number of shells which means the distance between nucleus and electron increases The electron to be added will experience more shielding down the group The halogen's oxidizing power(ability to accept an electron) decreases down the group
iii	Reactivity decreases down the group as the outershell electron gets further away from the nucleus and are more shielded by the inner electrons So it is harder for the halogen to attract and accept electrons
8.25	understand the trend in reactivity of Group 7 elements in terms of the redox reactions of Cl_2, Br_2 and I_2 with halide ions in aqueous solution *Students are expected to know the colours of the elements in standard conditions, in aqueous solution and in a non-polar organic solvent.*

	Chlorine (Cl_2)	Bromine (Br_2)	Iodine (I_2)
Potassium chloride (KCl)	X	No reaction	No reaction
Potassium bromide (KBr)	Chlorine displaces the bromide ions. Yellow–orange colour of bromine is seen	X	No reaction
Potassium iodide (KI)	Chlorine displaces the iodide ions. Brown colour of iodine is seen	Bromine displaces the iodide ions:. Brown colour of iodine is seen	X

Bromine is yellow-orange in solution and in non-polar organic solvent such as cyclohexane (which is useful as the halogens are more soluble in this layer)
Iodine is brown in solution but purple in non-polar organic solvent

8.26	understand, in terms of changes in oxidation number, the following reactions of the halogens: i oxidation reactions with Group 1 and 2 metals (redox reactions) ii the disproportionation reaction of chlorine with water and the use of chlorine in water treatment iii the disproportionation reaction of chlorine with cold, dilute aqueous sodium hydroxide to form bleach iv the disproportionation reaction of chlorine with hot alkali (70°C) v reactions analogous to those specified above
i	Halogens react with Gp.1 and 2 metals to form metal halide salts (ionic compounds that are usually white) The halogens act as oxidizing agents and the metals are being oxidized - Reactions are most vigorous between metals at the bottom of Gp.1 and 2 with the elements at the top of Gp.7 s
ii	A **disproportionation reaction** is a reaction in which an element in a single species is being simultaneously oxidized and reduced  Chloric(I)acid formed sterilizes water by killing bacteria
iii	Reaction goes like this: $Cl_2(aq) + 2NaOH(aq) \rightarrow NaCl(aq) + NaClO(aq) + H_2O(l)$  This is a disproportionation reaction as chlorine is being simultaneously oxidized and reduced Chlorine gets oxidized as there is an increase in oxidation number from 0 in Cl_2 to +5 in ClO_3^- Chlorine gets reduced as there is a decrease in oxidation number from 0 in Cl_2 to -1 in Cl^-
iv	Reaction goes like this: $3Cl_2(aq) + 6NaOH(aq) \rightarrow 5NaCl(aq) + NaClO_3(aq) + 3H_2O(l)$  Chlorine gets oxidized as there is an increase in oxidation number from 0 in Cl_2 to +5 in ClO_3^- Chlorine gets reduced as there is a decrease in oxidation number from 0 in Cl_2 to -1 in Cl^-

v

Reactions of Cl^-, Br^-, I^- ions with concentrated sulfuric acid

General Equation: $H_2SO_4(l) + X^-(aq) \rightarrow HX(g) + HSO_4^-(aq)$

You should know these typical observations made and products formed when sulfuric acid is added to the three halides

It doesn't have to be NaCl but also KCl or KBr

Halide	Observations	Products
NaCl	misty fumes	Hydrogen chloride, HCl
NaBr	misty fumes brown fumes colorless gas with choking smell	Hydrogen bromide, HBr Bromine, Br_2 Sulfur dioxide, SO_2
NaI	misty fumes purple fumes or black solid colorless gas with choking smell yellow solid colorless gas with rotten egg smell	Hydrogen iodide, HI Iodine, I_2 Sulfur dioxide, SO_2 Sulfur, S Hydrogen sulfide, H_2S

8.27

understand the following reactions:

i solid Group 1 halides with concentrated sulfuric acid, to illustrate the trend in reducing ability of the hydrogen halides

ii precipitation reactions of the aqueous anions Cl^-, Br^- and I^- with aqueous silver nitrate solution and nitric acid, and the solubility of the precipitates in aqueous ammonia solution

iii hydrogen halides with ammonia gas (to produce ammonium halides) and with water (to produce acids)

i

OXIDISING POWER	HALOGEN		HALIDE		REDUCING POWER
High ↑	fluorine	F_2	fluoride	F^-	Low ↓
	chlorine	Cl_2	chloride	Cl^-	
	bromine	Br_2	bromide	Br^-	
	iodine	I_2	iodide	I^-	
Low	astatine	At_2	astatide	At^-	High

Check out 2022 Jan U2 6 marker

ii

Halide Ion Tests!

Add dilute nitric acid and then add silver nitrate solution to the unknown solution, followed by ammonia solution

The halide ions will react like this:

$Ag^+(aq) + X^-(aq) \rightarrow AgX(s)$

	Cl^- ions	Br^- ions	I^- ions
Add silver nitrate solution	White precipitate	Cream precipitate	Yellow precipitate
Add dilute aq. ammonia	soluble	insoluble	insoluble
Add concentrated aq. ammonia	soluble	soluble	insoluble

iii

Hydrogen halides react with ammonia gas to produce ammonium halides

$HCl(g) + NH_3(g) \rightarrow NH_4Cl(s)$

Hydrogen halides react with water to produce acids

- Hydrogen chloride dissolves in water to form hydrochloric acid

8.28

be able to make predictions about fluorine and astatine and their compounds, in terms of knowledge of trends in halogen chemistry

You can use the trends to make predictions but do note this exception:

AgF is soluble so we cannot use silver nitrate solution to test for F^- ions

	Further suggested practicals: i reaction of solid potassium halides with concentrated sulfuric acid ii precipitation reaction for halides and other anions